Catalytic trimerization of ethene with highly active cyclopentadienyl-arene titanium catalysts

Deckers, P.J.W.; Hessen, B.; Teuben, J.H

Published in:
Organometallics

DOI:
10.1021/om020765a

Publication date:
2002

Catalytic Trimerization of Ethene with Highly Active Cyclopentadienyl−Arene Titanium Catalysts

Patrick J. W. Deckers, Bart Hessen,* and Jan H. Teuben

Dutch Polymer Institute/Center for Catalytic Olefin Polymerization, Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen, Nijenborgh 4, NL-9747AG Groningen, The Netherlands

Received September 13, 2002

The mono(cyclopentadienyl−arene)titanium complexes [η^5-C_5H_3R−(bridge)−Ar]$TiCl_3$, activated by methylalumoxane (MAO) cocatalyst, form a family of highly active catalysts for the trimerization of ethene, giving 1-hexene as the main product. Concomitant cotrimerization of ethene and 1-hexene, to give mainly 5-methylnon-1-ene, is also observed. The selectivity for trimerization depends on the presence of a pendant arene group on the cyclopentadienyl ligand and the nature of the bridge between these two ligand moieties. In the absence of a pendant arene, polyethene is the main product. The highest activity and selectivity for trimerization was observed for catalysts with a disubstituted C_1 bridge between the cyclopentadienyl and arene ligand moieties. A $SiMe_3$ substituent on the cyclopentadienyl ligand improves catalyst activity and selectivity, whereas methyl substitution of the arene decreases activity. Nevertheless, combining cyclopentadienyl $SiMe_3$ substitution with arene Me substitution gives rise to a catalyst with the highest activity and selectivity, evidence of the strongly nonlinear additivity of ligand substituent effects in this system. The cyclopentadienyl−arene ligand is likely to exhibit hemilabile behavior during catalysis, stabilizing intermediates by η^6 coordination and dissociating or slipping to make room for the incoming substrate. The presence of two pendant arene groups on the cyclopentadienyl ligand diminishes the activity of the catalyst but greatly enhances its stability.

Introduction

Linear 1-alkenes are important chemical intermediates that are used in the production of detergent alcohols (C_6−C_{16}) and synthetic lubricants, and as comonomers in the production of linear low-density polyethene (LLDPE, C_6 and C_8).[1] They are largely synthesized by catalytic oligomerization of ethene, yielding a Flory−Schultz distribution of chain lengths.[2] The selective synthesis of one specific linear alkene from ethene would be very attractive but (apart from the trivial dimerization of ethene to 1-butene)[3] is difficult to perform catalytically. The selective trimerization of ethene to give 1-hexene as the main product can be achieved with chromium Ziegler-type catalysts, consisting of a combination of Cr(III) salts (usually carboxylates) with aluminum alkyls in conjunction with some Lewis basic donor (especially pyrroles or 1,2-diethoxyethane).[4] The precise nature of the active species in these catalysts is as yet unknown, and it is difficult to control catalyst performance by well-directed catalyst modifications, although a recent report on diphosphine/$CrCl_3$/MAO catalysts showed strong ligand effects on catalyst activity and selectivity.[5] Two catalyst systems for the trimerization of ethene based on group 5 metals (V,[6] Ta)[7] have been reported, but the activities of these catalysts are orders of magnitude lower than those of the Cr-based Ziegler-type catalysts.

* To whom correspondence should be addressed. E-mail: hessen@chem.rug.nl.

(1) Vogt, D. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; p 245. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992; p 56.

(2) For examples, see: (a) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613. (b) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325. (c) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (d) Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21. (e) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65. (f) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005. (g) Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J. *Chem. Eur. J.* **2000**, *6*, 2221.

(3) For examples of ethene (and α-olefin) dimerization, see: (a) Muthukumaru Pillai, S.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86*, 353. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992; p 72. (c) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; p 258. (d) Britovsek, G. J. P.; Keim, W.; Mecking, S.; Sainz, D.; Wagner, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1632. (e) Christoffers, J.; Bergman, R. G. *Inorg. Chim. Acta* **1998**, *270*, 20. (f) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (g) Hauptman, E.; Sabo-Etienne, S.; White, P. S.; Brookhart, M.; Garner, J. M.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038.

(4) (a) Briggs, J. R. U.S. Pat. Appl. 4668838, 1987. (b) Karol, F. J.; Levine, I. J. U.S. Pat. Appl. 4777315, 1988. (c) Reagan, W. K.; Conroy, B. K. Eur. Pat. Appl. EP-416304, 1990. (d) Reagan, W. K.; Conroy, B. K. U.S. Pat. Appl. 5198563, 1993. (e) Tamura, M.; Uchida, K.; Iwanaga, K.; Ito, Y. Eur. Pat. Appl. EP-699648, 1995. (f) Reagan, W. K.; Pettijohn, T. M.; Freeman, J. W. U.S. Pat. Appl. 5523507, 1996. (g) Araki, Y.; Nakamura, H.; Nanba, Y.; Okano, T. U.S. Pat. Appl. 5856612, 1997. (h) Wu, F.-J. U.S. Pat. Appl. 5744677, 1998. (i) Wu, F.-J. U.S. Pat. Appl. 5968866, 1999. (j) Wass, D. F. PCT Int. Appl. WO 0204119, 2002.

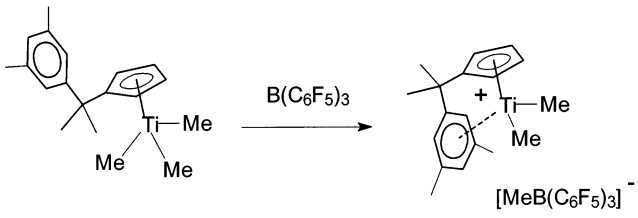
(5) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858.

(6) Romano, A. M.; Proto, A.; Santi, R.; Sommazzi, A.; Grande, M.; Masi, F. PCT Int. Appl. WO 0168572, 2001.

(7) Andes, C.; Harkins, S. B.; Murtuza, S.; Oyler, K.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 7423.

10.1021/om020765a CCC: $22.00
Publication on Web 10/19/2002

Scheme 1



Recently, we communicated that a mono(cyclopentadienyl)titanium catalyst system activated by methylalumoxane (MAO) cocatalyst, (η^5-$C_5H_4CMe_2Ar$)$TiCl_3$/MAO (Ar = Ph, 3,5-$Me_2C_6H_3$), is able to trimerize ethene with high activity.[8] The active species appear to be cationic titanium complexes in which the pendant arene group coordinates to the metal center[9] and in which the cyclopentadienyl−arene ancillary ligand displays hemilabile behavior. We observed earlier that reaction of the neutral (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)$TiMe_3$ complex with the Lewis acid $B(C_6F_5)_3$ affords the cationic species [(η^5:η^6-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)$TiMe_2$]$^+$, in which the arene moiety is coordinated to the titanium center (Scheme 1). In the presence of the Lewis base THF, the arene moiety is displaced to give a [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)-$TiMe_2(THF)_x$]$^+$ cationic species, thus behaving as a substitutionally labile group.[10]

In this paper we describe the synthesis of a range of (cyclopentadienyl−arene)titanium catalysts and evaluate the effect of variations in the ligand system on the performance in ethene trimerization catalysis. It is shown that ligand variations can have a substantial effect on the catalyst performance (activity, selectivity, and stability). As a result of these studies, a proposal for the pathways of generation and action of the species responsible for the trimerization could be formulated, and catalysts have been obtained that can produce >100 kg of ethene trimerization product/(g of Ti) under mild reaction conditions (30 °C, 5 bar of ethene).

Results and Discussion

Description and Synthesis of the Catalysts. The titanium complexes used in this study can all be described by the general formula [η^5-C_5H_3R−(bridge)−Ar]$TiCl_3$. These mono(cyclopentadienyl)titanium trichlorides can be converted into the cationic active catalyst species by reaction with methylalumoxane (MAO) cocatalyst. Alternatively, they can first be transformed into their trimethyl derivatives, which can then be reacted with various activators (Lewis acidic boranes, Brønsted acid, or trityl salts of weakly coordinating anions) that are commonly used with single-site olefin polymerization catalysts.[11]

The routes employed for the synthesis of the [η^5-C_5H_3R−(bridge)−Ar]$TiCl_3$ compounds are summarized in Scheme 2. Cyclopentadienyl ligands with $-CR_2Ar$ (R = alkyl, Ar = aryl) substituents are readily accessible from the reaction of 6,6-dialkylfulvenes with the appropriate aryllithium salts.[12] The resulting lithium cyclopentadienides, [$C_5H_4CR_2Ar$]Li, can be optionally quenched with trimethylsilyl chloride to afford the corresponding ($C_5H_4CR_2Ar$)$SiMe_3$ reagents.[9a] Introduction of a $-SiMe_2Ph$ or $-CH_2Ph$ moiety on the cyclopentadienyl ligand can be achieved by reaction of CpLi with dimethylphenylsilyl chloride ($PhMe_2SiCl$)[9a] or benzyl chloride,[13] respectively, to give $C_5H_5SiMe_2Ph$ or C_5H_5-CH_2Ph. Subsequent lithiation with *n*-BuLi affords the corresponding lithium salts. Reaction of 6-phenyl-6-methylfulvene with LDA (lithium diisopropylamide) gives [$C_5H_4C(=CH_2)Ph$]Li.[14] All lithium salts and (trimethylsilyl)cyclopentadienyl reagents were characterized by NMR spectroscopy.

The various (cyclopentadienyl)titanium trichlorides are readily prepared either via salt metathesis of the appropriate (cyclopentadienyl)lithium reagent with $TiCl_4$ in methylene chloride[10] or via Me_3SiCl elimination upon reaction of the appropriate (trimethylsilyl)cyclopentadienyl reagent with $TiCl_4$.[9a] All titanium compounds were characterized by ^1H and ^{13}C NMR spectroscopy and microanalysis.

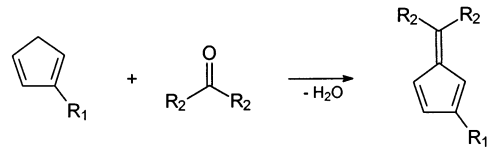
Ethene Trimerization with (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ (1)/MAO. The results of catalytic ethylene conversion experiments with the catalyst system (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ (**1**)/MAO (toluene solvent, Ti:Al ratio of 1:1000) under various conditions are listed in Table 1. Analysis of the liquid fraction by GC (using cyclooctane as internal standard), GC/MS, and NMR techniques revealed that, under these conditions, the catalyst produces olefin trimerization products with high selectivity (>95 wt % overall). These trimerization products consist of two fractions: C_6 (trimers of ethene) and C_{10} (cotrimers of ethene and 1-hexene, vide infra). In addition to the trimerization products, smaller amounts of C_8 (1 wt %) and polyethene (PE, 1−3 wt %) are produced.

The rate of production of 1-hexene increases with increasing ethene pressure. The C_6 productivity is around 550−600 kg/((mol of Ti) bar h) over a range of 2−10 bar of ethene pressure. Although no true kinetic studies were undertaken, the roughly linear dependence between the amount of C_6 product formed over the fixed run time of 30 min and the ethene pressure suggests that the rate of the trimerization process has a first-order dependence on the ethene concentration.

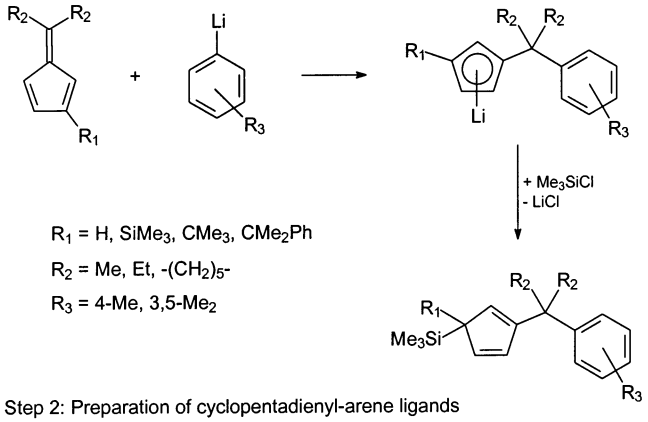
The C_6 product fraction consists predominantly of 1-hexene (99.5%), with the remaining 0.5% being a mixture of 2- and 3-hexenes. For entry 2 in Table 1, the C_{10} fraction was isolated by evaporation of the low-boiling (bp <80 °C at 180 Torr) volatile components of the reaction mixture and analyzed separately by NMR and GC/MS.[15] ^1H NMR analysis of the olefinic residues in this mixture indicates the presence of 90% $RCH_2CH=CH_2$ end groups, 5% RCH=CHR′, and 5% RR′C=CH_2.

(8) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2516.
(9) (a) Sassmannshausen, J.; Powell, A. K.; Anson, C. E.; Wocadlo, S.; Bochmann, M. *J. Organomet. Chem.* **1999**, *592*, 84. (b) Longo, P.; Amendola, A. G.; Fortunato, E.; Boccia, A. C.; Zambelli, A. *Macromol. Rapid Commun.* **2001**, *22*, 339. (c) Schwecke, C.; Kaminsky, W. *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 2805. (d) Flores, J. C.; Wood, J. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15*, 4944.
(10) Deckers, P. J. W.; Van der Linden, A. J.; Meetsma, A.; Hessen, B. *Eur. J. Inorg. Chem.* **2000**, 929.
(11) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.
(12) Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *148*, 35.
(13) Erker, G.; Aul, R. *Chem. Ber.* **1991**, *124*, 1301.
(14) Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Krüger, C.; Noe, R. *J. Am. Chem. Soc.* **1991**, *113*, 7594.
(15) The yield of the C_{10} fraction was 3.8 g, including some residual toluene solvent and cyclooctane standard, as seen by NMR.

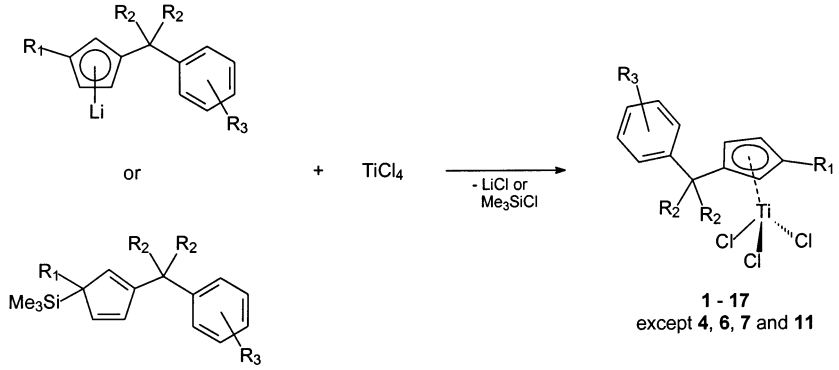
Scheme 2



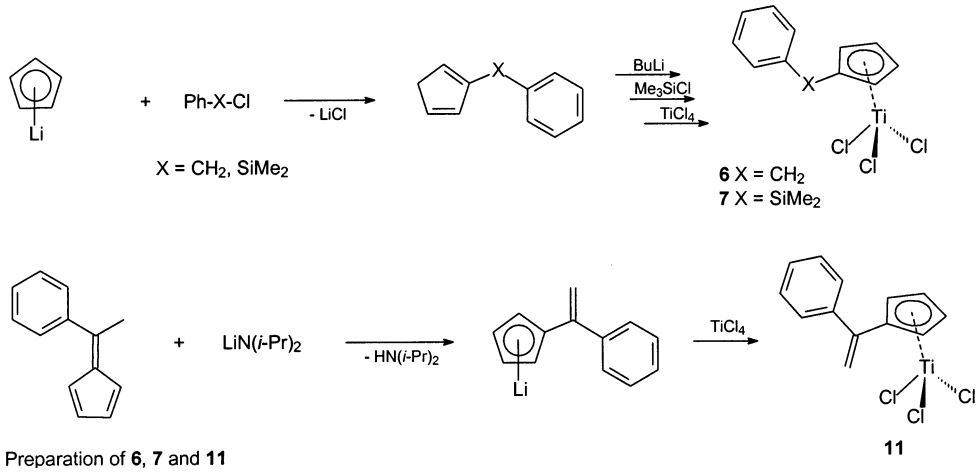
Step 1: Preparation of fulvenes



Step 2: Preparation of cyclopentadienyl-arene ligands



Step 3: Preparation of monocyclopentadienyl-arene titanium trichlorides



Preparation of **6**, **7** and **11**

GC/MS indicates that the C_{10} fraction mainly consists of 5-methylnon-1-ene (83%). The only detectable product in the C_8 fraction (by GC) is 1-octene. DSC analyses of the polyethene samples gave melting points higher than 128 °C, indicative of HDPE (high-density polyethene),[16] suggesting that very little of the 1-hexene formed is incorporated into the polymer.

The thermal stability of the catalyst system **1**/MAO is modest (Table 2): increasing the reaction temperature decreases the overall catalyst productivity over the 30 min run period and increases the relative amount of PE produced. This is likely to be associated with catalyst

(16) Karol, F. J. *CHEMTECH* **1983**, 222.

Table 1. Catalytic Ethene Conversion with the 1/MAO Catalyst System as a Function of Ethene Pressure[a]

P(ethene), bar	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
2	8.0 (87)	1.0 (11)	0.2 (1.6)	535	98	41
5	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110
10	47.2 (86)	5.1 (9)	1.4 (2.6)	630	95	239

[a] Reaction conditions: toluene solvent, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

Table 2. Catalytic Ethene Conversion with the 1/MAO Catalyst System as a Function of Temperature[a]

T, °C	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
30	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110
50	12.4 (83)	1.6 (11)	0.7 (4.6)	330	94	64
80	3.3 (76)	0.2 (4)	0.8 (19)	90	80	17

[a] Reaction conditions: toluene solvent, 5 bar of ethene pressure, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

Table 3. Catalytic Ethene Conversion with the 1/MAO Catalyst System in the Presence of Added 1-Octene[a]

P(ethene), bar	1-octene, g	C_6 products, g (wt %)	C_{10} products, g (wt %)	C_{12} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
2	0	8.0 (87)	1.0 (11)	0.03 (0.4)	0.2 (1.6)	535	98	41
2	15	6.3 (69)	0.7 (8)	2.0 (22)	0.1 (1.1)	425	99	37
5	0	20.9 (83)	3.5 (14)	0.1 (0.4)	0.5 (1.8)	555	97	110
5	15	16.6 (75)	2.2 (10)	2.7 (12)	0.5 (2.3)	445	97	92

[a] Reaction conditions: toluene solvent, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

Table 4. Catalytic Ethene Conversion with the (η^5-$C_5H_4CMe_2R$)$TiCl_3$/MAO Catalyst Systems[a]

catalyst (R)	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
1 (Ph)	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110
2 (4-MeC_6H_4)	14.7 (88)	1.6 (10)	0.3 (1.6)	395	98	75
3 (3,5-$Me_2C_6H_3$)	7.9 (93)	0.1 (4)	0.1 (1.3)	210	97	38
4 (Me)	0.5 (17)	0.1 (4)	2.4 (76)	13	21	3

[a] Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

degradation, as suggested by the more rapid decrease in ethene uptake rate during the runs at elevated temperature. At 80 °C, ethene uptake stops completely after about 10 min of reaction time, whereas at 30 °C ethene is consumed over the whole run period, although the uptake rate does slow gradually over the course of the run.

The C_{10} product fraction is likely to be produced by cotrimerization of ethene and 1-hexene rather than by direct pentamerization of ethene. In separate experiments, ethene was converted by the catalyst **1**/MAO at 30 °C in the presence of 15 g of 1-octene added to the reaction mixture (Table 3). In addition to the C_6 and C_{10} product fractions mentioned above, a considerable amount of C_{12} products (cotrimers of ethene and 1-octene, obtained in 2−3 g quantities, depending on the ethene pressure) is now observed as well. This is likely to stem from ethene/1-octene cotrimerization, and these results indicate that the C_{10} product fraction in the catalytic ethene oligomerization by **1**/MAO is indeed formed via cotrimerization of ethene and 1-hexene.

Effect of the Pendant Arene Group on Ethene Trimerization Catalysis. The effect of the pendant arene group on ethene conversion by the (η^5-$C_5H_4CMe_2$-Ar)$TiCl_3$/MAO catalysts was probed by studying the catalysts with Ar = Ph (**1**), 4-MeC_6H_4 (**2**), 3,5-$Me_2C_6H_3$ (**3**) and comparing them with an analogous system without a pendant arene, (η^5-$C_5H_4CMe_3$)$TiCl_3$ (**4**). The results are listed in Table 4.

It can be seen that making the pendant phenyl group more electron-rich, by adding one or two methyl substituents, respectively, significantly diminishes the productivity of the catalyst with each methyl group added, whereas the selectivity for trimerization is retained. This reduction of catalyst productivity upon methyl substitution of the pendant group reflects a slowing down of the catalytic cycle, as no evidence was found for a more rapid catalyst deactivation in these systems. The absence of the pendant arene group leads to the predominant formation of polyethene, indicating that the pendant arene group is essential to obtaining selective trimerization. These observations suggest that the cyclopentadienyl−arene ligand is likely to display hemilabile character in the course of the catalysis: it has to be present for coordination, apparently helping to generate the species responsible for the selective trimerization, but if it binds too strongly it can slow the catalytic reaction.

It may be noted that even for the *tert*-butylcyclopentadienyl system **4**/MAO a certain amount of ethene trimerization product is observed in addition to the main product, polyethene. A related observation was made recently by Pellecchia and co-workers in ethene polymerization with the [(η^5-C_5Me_5)$TiMe_2$][$MeB(C_6F_5)_3$] catalyst in toluene solvent, where the PE obtained contains a noticeable amount of *n*-butyl side groups[17] It was suggested that the catalyst is partly converted to a species that trimerizes ethene to 1-hexene, which is then

Table 5. Catalytic Ethene Conversion with the 1/MAO Catalyst System in Two Different Solvents[a]

toluene, vol %	*n*-octane, vol %	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
100	0	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110
20	80	8.1 (87)	0.8 (9)	0.4 (4.3)	215	96	41

[a] Reaction conditions: 5 bar of ethene pressure, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

incorporated into the polymer. Our observations indicate that transient coordination of the toluene solvent to the metal center may be instrumental in this,[18] albeit less efficient than the pendant arene group in the (η^5-C_5H_4-CMe_2Ar)$TiCl_3$/MAO systems, as the interaction is intermolecular rather than intramolecular.

To estimate the possible role of solvent interactions on the selective ethene trimerization by the (cyclopentadienyl−arene)titanium catalysts, we investigated the catalyst system **1**/MAO in an 80:20 (v/v) mixture of *n*-octane and toluene (Table 5). The ethene conversion results showed that the selectivity for trimerization is largely retained but that the catalyst productivity over the 30 min run is lower than in neat toluene. The initial ethene uptake rate is identical with that of the corresponding run in neat toluene, but the catalyst appears to deactivate more rapidly in the *n*-octane/toluene mixture. These findings indicate that the intrinsic trimerization process and its selectivity do not depend on the aromatic solvent but that having an aromatic solvent may be beneficial for the catalyst stability.

Proposed Catalytic Cycle for Ethene Trimerization. It has been proposed that the only family of catalysts known thus far to perform efficient and selective ethene trimerization (Ziegler-type catalysts based on the combination of chromium salts with aluminum alkyls and added Lewis bases)[4] acts through a mechanism involving metallacyclic intermediates. This may proceed through initial oxidative coupling of two ethene molecules by a low-valent chromium species, generated in situ, to produce a chromacyclopentane compound. Insertion of an additional ethene molecule into one of the Cr−C bonds then affords a chromacycloheptane species. Subsequent β-H abstraction and reductive elimination can then lead to the formation of 1-hexene and the regeneration of the low-valent chromium species.[19]

This sequence explains the lack of 1-butene formation, as the chromacyclopentane is expected to be much more stable toward β-H abstraction than the more flexible chromacycloheptane.[20] For the very recently reported selective ethene trimerization by $TaMe_2Cl_3$, a similar catalytic cycle via metallacycles has been proposed.[7]

It is likely that a similar mechanism is operative in the selective trimerization performed by the (cyclopentadienyl−arene)titanium catalysts presented here, involving cationic Ti(IV) metallacyclic intermediates and the Ti(II)/Ti(IV) couple for oxidative coupling/reductive elimination. Several catalytic C−C coupling reactions have been reported in neutral titanium systems that involve metallacyclic intermediates and a Ti(II)/Ti(IV) couple.[21] It is less obvious how the required (cationic) low-valent Ti(II) species would be generated from a mono(cyclopentadienyl)titanium(IV) trichloride complex and MAO.

One possibility is that the cationic $[(Cp-arene)Ti(CH_2CH_2R)_2]^+$ species, likely to be generated initially by alkylation of the (Cp−arene)$TiCl_3$ by MAO followed by alkyl anion abstraction and sequential ethene insertions into the Ti-Me bonds, is in equilibrium with its hydride-olefin isomer $[(Cp-arene)Ti(H)(\eta^2\text{-}CH_2{=}CHR)(CH_2CH_2R)]^+$. This may be followed either by dissociation of the alkene (to yield a cationic hydrido alkyl Ti(IV) intermediate that is likely to undergo subsequent reductive elimination of the alkane to give a cationic Ti(II) species) or by reductive elimination of the alkane (to yield a cationic Ti(II) olefin complex). In both pathways, the coordination of the arene moiety can provide additional stabilization to the Ti(II) state. Presently it is impossible for us to distinguish between the two pathways (although the latter appears to be the more likely, as it avoids the formation of a "naked" cationic (Cp−arene)Ti(II) species). A theoretical study of the process using DFT calculations is presently in progress. The catalytic cycle as proposed on the basis of the information available at this moment is summarized in Scheme 3.

If the rate of 1-hexene formation is indeed first order in ethene (vide supra), it is very likely that the insertion of the third ethene molecule into one of the metal−carbon bonds of the proposed 16-electron cationic titanacyclopentane intermediate is the rate-determining step. This reaction will require the displacement or slippage of the η^6-coordinated arene ligand to yield a less electron-rich metal center that can capture and insert the third ethene molecule. It is thus possible that the process of arene dissociation or ring slippage from a cationic Ti(IV) species is involved in the rate-determining step, which would be consistent with the observed decrease in catalyst activity upon increasing the donor ability of the pendant arene group.

Kinetic studies of chromium-based ethene trimerization catalysts have revealed a second-order rate dependence on ethene concentration, indicating that in these systems the formation of the chromacyclopentane (or a bis(ethene) adduct leading to this species) is likely to be rate-determining.[22] However, the selective trimerization of 1-hexene with triazacyclohexane−chromium catalysts was recently reported to have as a rate-

(17) Pellecchia, C.; Pappalardo, D.; Gruter, G. J. *Macromolecules* **1999**, *32*, 4491.
(18) Gillis, D. J.; Tudoret, M. J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543.
(19) Briggs, J. R. *J. Chem. Soc., Chem. Commun.* **1989**, 674.
(20) Emrich, R.; Heinemann, O.; Jolly, P. W.; Krüger, C.; Verhovnik, G. P. J. *Organometallics* **1997**, *16*, 1511.
(21) (a) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630. (b) Waratuke, S. A.; Thorn, M. G.; Fanwick, P. E.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1999**, *121*, 9111.
(22) (a) Manyik, R. M.; Walker, W. E.; Wilson, T. P. *J. Catal.* **1977**, *47*, 197. (b) Yang, Y.; Kim, H.; Lee, J.; Paik, H.; Jang, H. G. *Appl. Catal. A: Gen.* **2000**, *193*, 29.

Scheme 3

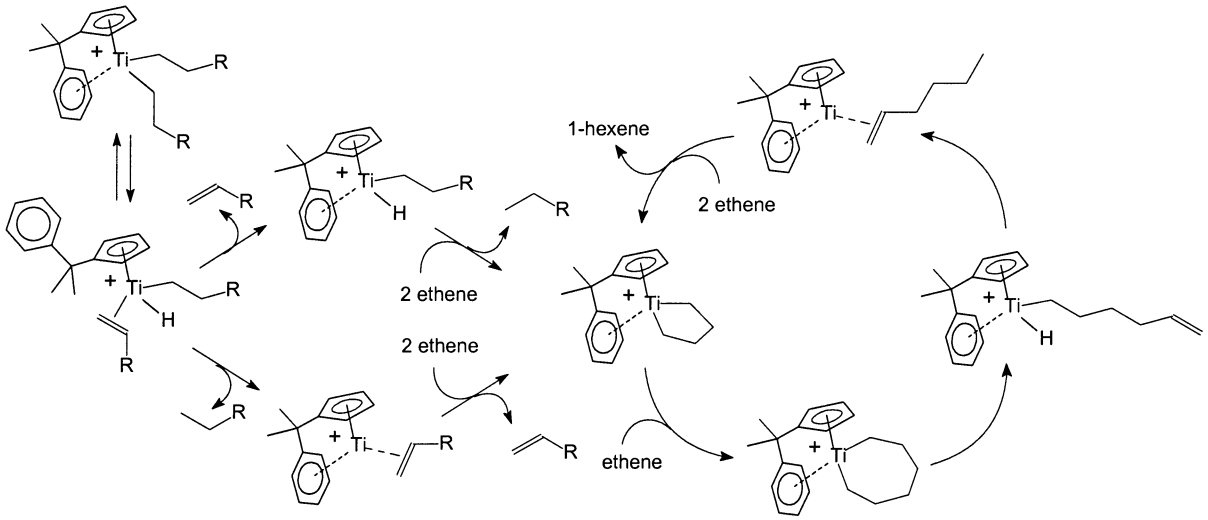


Table 6. Catalytic Ethene Conversion with 5/Cocatalyst Systems Compared with 1/MAO[a]

cocatalyst	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
$[PhNMe_2H][B(C_6F_5)_4]$[d]	14.6 (90)	1.2 (7)	0.3 (2.0)	390	97	73
$B(C_6F_5)_3$[d]	5.8 (88)	0.3 (5)	0.4 (6)	155	93	29
MAO/SiO_2[e]	13.8 (95)	0.6 (4)	n.d.	365	99[f]	68
1/MAO[g]	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110

[a] Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h). [d] B:Ti ratio = 1.1. [e] 5 wt % MAO on silica, Al:Ti ratio = 250. [f] Product distribution is based on liquid fraction only (remaining 1 wt % is C_8 and C_{12+} fractions). [g] Al:Ti ratio = 1000.

determining step the insertion of the third monomer molecule.[23]

Zhu and co-workers reported recently that the catalyst system (η^5-C_5Me_5)$Ti(OCH_2Ph)_3$/MAO in heptane produces short chain (ethyl and butyl) branched polyethene in the homopolymerization of ethene, and they proposed a reduced titanium species as being responsible for in situ dimerization and trimerization of ethene.[24] They suggest that free $AlMe_3$, present in MAO, is essential in the reduction of titanium(IV) and the subsequent oligomerization of ethene. Decreasing the $AlMe_3$ amount in the cocatalyst indeed diminishes the degree of branching in the PE obtained with this catalyst system. The presence of ethyl branches (in addition to butyl branches) in the polyethene generated by the (η^5-C_5Me_5)$Ti(OCH_2Ph)_3$/MAO catalyst suggests that a different oligomerization mechanism is at work in this particular system, as neither with the (η^5-C_5Me_5)-$TiMe_3/B(C_6F_5)_3$/toluene catalyst[17] nor with the (Cp−arene)$TiCl_3$/MAO systems described here have indications for the formation of significant amounts of 1-butene been found.

To evaluate the effect of the cocatalyst on the trimerization catalysis, we performed catalytic ethene conversion studies using (η^5-$C_5H_4CMe_2Ph$)$TiMe_3$ (**5**), with the cocatalysts $[PhNMe_2H][B(C_6F_5)_4]$, $B(C_6F_5)_3$, and MAO/SiO_2 (Table 6). All catalyst systems show predominant formation of trimerization products, indicating that free $AlMe_3$ is not instrumental in the generation of the species that produces 1-hexene. MAO/SiO_2 and $[PhNMe_2H][B(C_6F_5)_4]$ proved to be efficient cocatalysts, affording active and highly selective (>97 wt %) trimerization catalysts. The selectivity of the **5**/$B(C_6F_5)_3$ catalyst system is slightly worse (about 93 wt % of trimerization products), and its activity is rather low. This may be associated with the relatively strong coordinative ability of the $[MeB(C_6F_5)_3]^-$ anion.[25] It may be taken into account that the experiments with the $B(C_6F_5)_3$ and $[PhNMe_2H][B(C_6F_5)_4]$ activated systems are conducted in the absence of impurity scavenger, which might partially explain the lower activities, compared to **1**/MAO.

Effect of the Bridge between the Cyclopentadienyl and Arene Groups. To probe structure−performance relationships in the (Cp−arene)Ti-based ethene trimerization catalyst system, the effect of the bridge between the cyclopentadienyl ligand and the arene group on catalytic ethene conversion was investigated. The precatalysts (η^5-$C_5H_4CH_2Ph$)$TiCl_3$ (**6**), (η^5-C_5H_4-$SiMe_2Ph$)$TiCl_3$ (**7**), and (η^5-$C_5H_4CMe_2CH_2Ph$)$TiCl_3$ (**8**) were tested in ethene conversions with MAO activator and compared with the reference catalyst (η^5-$C_5H_4CMe_2$-Ph)$TiCl_3$ (**1**)/MAO (Table 7).

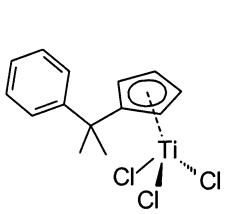
The catalysts with the CH_2 and $SiMe_2$ bridges (**6** and **7**, respectively) both produce 1-hexene and polyethene in comparable amounts, together with a Flory−Schulz

(23) (a) Köhn, R. D.; Haufe, M.; Kociok-Köhn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4337. (b) Mihan, S.; Lilge, D.; Maas, H.; Molnar, F.; Köhn, R.; Seifert, G.; Kociok-Köhn, G. *Abstracts of Papers*, 221st National Meeting of the American Chemical Society, San Diego, CA, April 2001; American Chemical Society: Washington, DC, 2001; INOR 114.

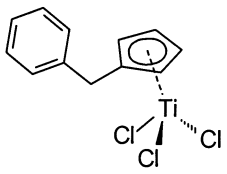
(24) Zhu, F.; Huang, Y.; Yang, Y.; Lin, S. *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 4258.

(25) For examples, see: (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (b) Bochmann, M.; Lancaster, S. J. *Organometallics* **1994**, *13*, 2235. (c) LaPointe, R. E.; Stevens, J. C.; Nickias, P. N.; Mark, M. H. Eur. Pat. Appl. EP-520732-A, 1992. For recent reviews, see: (d) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345. (e) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

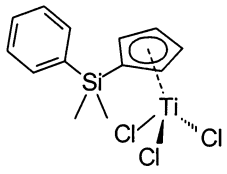
Table 7. Catalytic Ethene Conversion with the [η^5-C_5H_4−(B)−Ph]$TiCl_3$/MAO Catalyst Systems[a]



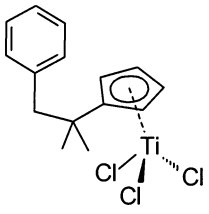
1



6



7

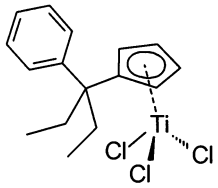


8

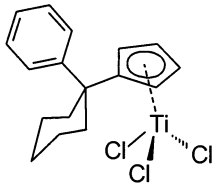
catalyst (B)	C_6 products, g (wt %)	C_8 products, g (wt %)	C_{10} products, g (wt %)	C_{12-24} products, g (wt %)	PE, g (wt %)	trimerizn products, wt %
1 (CMe_2)	20.9 (83)	0.3 (1)	3.5 (14)	0.1 (0.5)	0.5 (2)	97
6 (CH_2)	2.7 (42)	0.4 (6)	0.6 (9)	0.6 (9)	2.2 (34)	<51
7 ($SiMe_2$)	2.1 (36)	0.3 (5)	0.4 (7)	0.5 (8)	2.6 (44)	<43
8 (CMe_2CH_2)	1.2 (83)	0.1 (7)	0.05 (3)	0.01 (0.7)	0.1 (7)	86

[a] Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time.

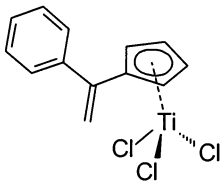
Table 8. Catalytic Ethene Conversion with the (η^5-$C_5H_4CR_2Ph$)$TiCl_3$/MAO Catalyst Systems[a]



9



10



11

catalyst (R_2)	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
1 (Me_2)	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110
9 (Et_2)	18.5 (88)	1.4 (7)	1.0 (4.6)	495	95	92
10 (−$(CH_2)_5$−)	24.4 (87)	2.9 (10)	0.6 (2.0)	650	97	125
11 (=CH_2)	17.3 (88)	1.4 (7)	0.9 (4.7)	460	95	87

[a] Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

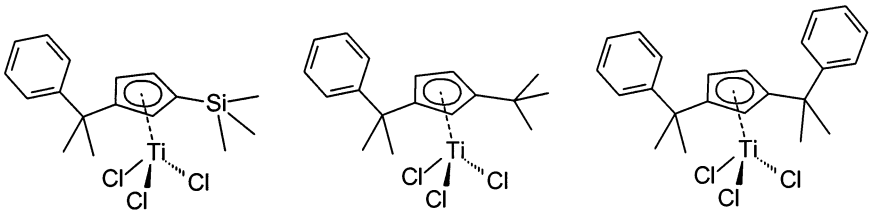
type distribution of higher 1-alkenes. These systems thus have a very poor selectivity for trimerization. The catalyst **8** (with a bridge with a C_2 backbone) produces mainly 1-hexene, but at a very slow rate.

From the above experiments it is clear that a disubstituted C_1 bridge between the cyclopentadienyl and arene moieties gives the best selectivity and activity in catalytic ethene trimerization. To refine this point further, we prepared three more precatalysts of the type [η^5-C_5H_4−(B)−Ph]$TiCl_3$ that satisfy this requirement: **9** (B = CEt_2), **10** (B = C[$(CH_2)_5$]), and **11** (B = C=CH_2). The data in Table 8 show that, upon activation with MAO, all these catalysts are indeed active and selective in ethene trimerization. The performance of **10**/MAO, with the bridging carbon forming part of a 1,1-disubstituted cyclohexane moiety, even exceeds that of the reference catalyst **1**/MAO, whereas the catalyst with the CEt_2 bridge is slightly inferior to its CMe_2 analogue in both activity and selectivity. Interestingly, the catalyst **11**/MAO, with an sp^2 bridging carbon, also performs reasonably well, with trimerization behavior comparable to that of the catalyst with the CEt_2 bridge.

From the data in Table 7, it can be seen that the bridging unit plays a crucial role in the selective ethene trimerization performance of these catalyst systems. The transformation of the catalyst from a species active in polymerization into one that is active in trimerization, as put forward in the in the proposed mechanism, involves the coordination of the arene moiety to the electron-deficient titanium center to generate the *ansa*-Cp−arene Ti(II) species (Scheme 3). Apparently, both the CH_2 (**6**) and $SiMe_2$ (**7**) bridged compounds are less effective in this respect than the CMe_2-bridged parent compound (**1**). It is as yet unclear whether this is the result of a slow switch from the polymerization catalyst (Ti(IV)−dialkyl) to the trimerization catalyst (Ti(II)/Ti(IV)−metallacycle), promoted by (intramolecular) arene coordination, or if the trimerization catalyst, once formed, can readily be transformed back into a species active in polymerization.

Catalyst precursors **1** and **6** have recently been compared in the polymerization of styrene.[9c] The **1**/MAO (CMe_2-bridged) system displayed significantly lower polymerization activity and afforded syndiotactic polystyrene with a lower molecular weight and melting temperature than the CH_2-bridged catalyst **6**/MAO, presumably due to stronger arene coordination in the cationic catalytic species derived from **1**. Different coordinating properties of the phenyl group in cationic metallocene species with $C_5H_4CR_2Ph$ ligands (R = H, Me) were also observed for cationic species generated from the reaction of (η^5-$C_5H_4CR_2Ph)_2ZrMe_2$ with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$.[26] Only for the cation with R = Me did NMR spectroscopy suggest some form of intramolecular coordination of the pendant phenyl group. These findings indicate that the formation of *ansa*-cyclopen-

Table 9. Catalytic Ethene Conversion with the [η^5-(3-R)$C_5H_3CMe_2Ph$]$TiCl_3$/MAO Catalyst Systems[a]



12 **13** **14**

catalyst (R)	time, min	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
1 (H)	30	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110
1 (H)	120	27.9 (78)	6.6 (18)	1.0 (2.8)	185	96	38
12 ($SiMe_3$)	30	25.2 (85)	3.3 (11)	0.4 (1.2)	670	96	130
13 (CMe_3)	30	14.7 (89)	0.9 (5)	0.7 (4.3)	390	94	73
14 (CMe_2Ph)	30	11.9 (91)	0.6 (5)	0.3 (2.3)	315	96	59
14 (CMe_2Ph)	120	46.6 (89)	4.1 (8)	0.8 (1.5)	310	97	59

[a] Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

tadienyl−arene Ti(II) cations, the prerequisite for selective ethene trimerization activity, is likely to be facile for the CMe_2-bridged species, which could explain the differences in ethene conversion for **1**/MAO and **6**/MAO.[27]

The catalyst performance of the $SiMe_2$-bridged species **7** is most likely related to the poor accessibility of the *ansa*-Cp−arene coordination mode of the ancillary ligand. Due to the larger ionic radius of silicon (0.26 Å) versus carbon (0.15 Å)[28] the ligand will have to adopt a much more acute Cp−Si−arene bend angle to accommodate ansa coordination.[29] Bochmann and co-workers reported that the reaction of (η^5-$C_5H_4SiMe_2Ph$)$TiMe_3$ with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ affords highly thermally labile species (even at −60 °C), in contrast to the much more stable complex [(η^5:η^6-$C_5H_4CMe_2Ph$)-$TiMe_2$][$B(C_6F_5)_4$], tentatively suggesting the absence of the crucial arene coordination in the former cationic species.[9a] These observations may indicate that in **7**/MAO the conversion from an ethene polymerization catalyst to an ethene trimerization catalyst is slow compared to that for **1**/MAO.

The clean formation of *ansa*-cyclopentadienyl−arene cationic titanium species for the reaction of the trimethyl derivative of **8**, (η^5-$C_5H_4CMe_2CH_2Ph$)$TiMe_3$, with $B(C_6F_5)_3$ [9a] (and for the reaction of (η^5-$C_5Me_4CH_2CH_2$-Ph)$TiMe_3$ with $[Ph_3C][B(C_6F_5)_4]$)[9d] suggests that the ansa coordination, crucial for trimerization selectivity, is readily accessible for bridges with a C_2 backbone. Accordingly, a relatively good trimerization selectivity of 86% is obtained for **8**/MAO, albeit at a slow rate. The longer, more flexible CMe_2CH_2 bridge probably allows for a stronger η^6-arene coordination in **8** than for **1** with the CMe_2 bridge.[30] The "constrained geometry" of the C_1-bridged *ansa*-(η^5: η^6-Cp−arene)Ti species might facilitate the slippage or dissociation of the arene ring, proposed for the rate-determining insertion of the third ethene molecule into the titanacyclopentane, resulting in a higher trimerization activity of **1**/MAO relative to **8**/MAO.

The differences in trimerization activity between the **1**/MAO, **9**/MAO, and **10**/MAO systems are relatively small (maximum 25%) and can be the result of the different steric properties of the backbone substituents[31] or other effects that influence the propensity for arene "ring slippage" in the proposed rate-determining step. Since *ansa*-cyclopentadienyl−arene coordination of the ancillary ligand is crucial to ethene trimerization reactivity (vide supra), the behavior of the [$C_5H_4C(=CH_2)$-Ph] ligand (**11**) is somewhat puzzling. To adopt the required conformation, the Cp−C−arene bend angle in this ligand has to be reduced even more from its unstrained value (around 120°) than for the nonselective $SiMe_2$-bridged species **7**. One possibility is that the unsaturated moiety in the bridge of **11** gets alkylated in the process, which would effectively turn it into a CRR′-bridged species. Further study of the cationic dialkyl derivative of **11** would be required to investigate this issue.

Effect of Substituents on the Cyclopentadienyl Group. The effect of the attachment of substituents on the cyclopentadienyl moiety of the cyclopentadienyl−arene catalysts was probed by the synthesis of three precatalysts of the type [η^5-(3-R)$C_5H_3CMe_2Ph$]$TiCl_3$: **12** (R = $SiMe_3$), **13** (R = CMe_3), and **14** (R = CMe_2Ph). The results of catalytic ethene conversion with these cata-

(26) (a) Bochmann, M.; Green, M. L. H.; Powell, A. K.; Sassmannshausen, J.; Triller, M. U.; Wocadlo, S. *J. Chem. Soc., Dalton Trans.* **1999**, 43. (b) Doerrer, L. H.; Green, M. L. H.; Haüssinger, D.; Sassmannshausen, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2111.

(27) Metal−arene interactions were proposed to explain the observation that in ethene polymerization with [η^5-C_5H_4−(B)−Ph]$_2ZrCl_2$/MAO systems (B = CH_2, CMe_2, $SiMe_2$), the CH_2- and $SiMe_2$-bridged species are about 20 times as active as the CMe_2-bridged species. See: Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205.

(28) *CRC Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1999; pp 12−14.

(29) For example, in the X-ray structures of $Me_2X(\eta^5$-$C_5H_4)ZrCl_2$ (X = C, Si) a difference of 6.3° is observed in the respective bend angles. See: (a) Koch, T.; Blaurock, S.; Somoza, F. B., Jr.; Voigt, A.; Kirmse, R.; Hey-Hawkins, E. *Organometallics* **2000**, *19*, 2556. (b) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

(30) The X-ray structure of {[(η^5:η^6-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(μ-Br)]$_2$}$[B(C_6F_5)_4]_2$ indicates that the arene moiety does not coordinate in a fully symmetrical η^6 fashion but that the three carbons closest to the bridge show shorter Ti−C distances than the other three (approaching η^3 coordination).[10]

(31) For examples of backbone substituent effects in *ansa*-metallocenes, see: (a) Razavi, A.; Atwood, J. L. *Macromol. Symp.* **1995**, *89*, 345. (b) Alt, H. G.; Zenk, R. *J. Organomet. Chem.* **1996**, *526*, 295. (c) Ewen, J. A.; Hapseslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544.

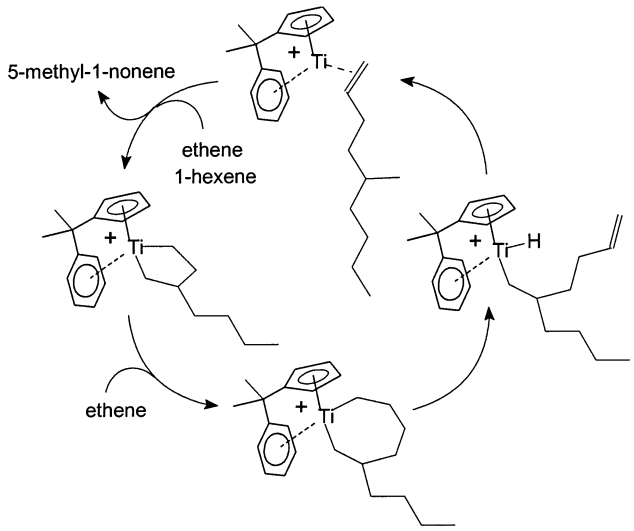
lysts using MAO activator, and comparative data for the reference catalyst **1**/MAO, are listed in Table 9.

As expected, all three systems show good selectivity for trimerization. The $SiMe_3$-substituted catalyst **12**/MAO shows a somewhat improved activity over **1**/MAO, but the CMe_3-substituted catalyst **13**/MAO exhibits a lower productivity and selectivity over the 30 min run period. This appears to be due to a catalyst degradation process in the latter system. Its initial ethene uptake rate is comparable to that of **12**/MAO but decreases much more rapidly over time, the catalyst being fully deactivated after 15 min. The catalyst **14**/MAO, which has two CMe_2Ph substituents on the cyclopentadienyl ring that, in principle, can both (alternately) coordinate to the metal center, is selective but rather slow compared to **1**/MAO. Nevertheless, the catalyst **14**/MAO does have a very interesting feature. As mentioned before, the thermal stability of **1**/MAO is only modest, and even at 30 °C catalyst degradation is taking place noticeably. The top two entries of Table 9 describe the behavior of **1**/MAO at run times of 30 and 120 min, respectively. It is clear that catalyst deactivation limits the total production attainable by this catalyst to around 48 kg of trimerization product/(g of Ti). In contrast, **14**/MAO displays a comparable productivity (around 310 kg of C_6/(mol h bar)) over both the 30 and 120 min runs, affording a production of 71 kg of trimerization product/(g of Ti) after 120 min, at which stage the catalyst is still active. Thus, the presence of two CMe_2Ph substituents slows down the catalysis but greatly improves catalyst stability. The increased stability may be related to our earlier observation that **1**/MAO degrades less rapidly in neat toluene solvent than in an *n*-octane/toluene (80/20 v/v) mixture, possibly indicating catalyst stabilization by transient toluene coordination. The lower activity may be caused by competition between the loose pendant arene substituent and incoming ethene on the titanacyclopentane intermediate.

The stabilities of the catalysts **12** (R = $SiMe_3$)/MAO and **13** (R = CMe_3)/MAO differ significantly. The actual deactivation mechanism is not known presently, but various possible pathways can be suggested. For instance, it is possible that electronic effects play a role in the stabilization of the catalytic species. As suggested earlier, (transient) arene coordination improves the catalyst stability. The electron-donating *tert*-butyl group of **13** increases the electron density on the titanium center, making it less prone to arene coordination and thus possibly more amenable to catalyst deactivation. A second possible deactivation pathway involves cyclometalation of the EMe_3 substituent (E = Si, **12**; E = C, **13**). Marks and co-workers reported that for cationic zirconocene species $[(\eta^5\text{-}C_5H_4R)(\eta^5\text{-}C_5H_4CMe_3)ZrR']^+$ this process occurs more easily for E = C than for E = Si.[25a] A similar trend in our systems could explain the greater stability of **12**/MAO relative to **13**/MAO in selective ethene trimerization.

The addition of a substituent on the cyclopentadienyl ring also affects the composition of the trimerization products formed. For the $SiMe_3$-substituted catalyst **12**/MAO the 1-hexene content of the C_6 fraction rises to 99.9% (99.7% for **1**/MAO) and the 5-methyl-1-nonene content of the C_{10} fraction to 92% (85% for **1**/MAO). For the *tert*-butyl-substituted catalyst **13**/MAO these trends are similar (99.8% and 91%, respectively).

Scheme 4



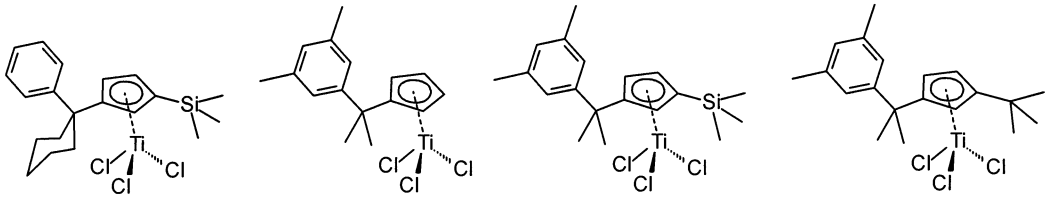
Considering all the possibilities to form C_{10} products from ethene and 1-hexene via the proposed trimerization mechanism, it appears that one pathway is by far the most favorable. This is illustrated in Scheme 4 and proceeds through selective oxidative coupling of ethene with 1-hexene to give a titanacylopentane with the *n*-butyl substituent on the β-carbon. This is followed by an insertion of ethene into the Ti−C bond at the unsubstituted side of the metallacycle, giving a β-*n*-butyl-substituted titanacycloheptane, which then affords 5-methylnon-1-ene via β-H transfer from the unsubstituted side of the metallacycle and reductive elimination.[32] The similar product distribution within the C_{10} fractions observed for the $SiMe_3$ (**12**) and CMe_3 (**13**) substituted catalysts suggests that the selectivity of the cotrimerization is mainly controlled by the steric properties of the substituted cyclopentadienyl ligand rather than by its electronic properties.

Combining Ligand Effects. The investigation of the effect of single ligand variations on the catalytic ethene conversion with (cyclopentadienyl−arene)titanium species (variation in bridging group, substituents on the cyclopentadienyl moiety, and substituents on the aryl moiety) has resulted in the identification of specific features that appear to be advantageous to catalyst efficiency. In comparison under standard conditions to the reference catalyst **1**/MAO, the catalyst with the $C[(CH_2)_5]$ bridging group (**10**) shows a 17% increase in C_6 productivity, and the catalyst with the $SiMe_3$-substituted cyclopentadienyl group (**12**) shows a 20% increase. Combining these features in the catalyst $\{\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3C[(CH_2)_5]Ph\}TiCl_3$ (**15**)/MAO leads to a 57% increase in C_6 productivity relative to **1**/MAO (Table 10). This suggests that the effects of variations in bridging group and cyclopentadienyl substituent are roughly additive, with a slightly positive nonlinearity.

In contrast to the positive effect on C_6 productivity of substitution on the cyclopentadienyl group, the attach-

(32) A similar pathway has been proposed for the cotrimerization of ethene with styrene with $[Cp^RTiMe_2]^+$ cations. See: Pellecchia, C.; Pappalardo, D.; Oliva, L.; Mazzeo, M.; Gruter, G. J. *Macromolecules* **2000**, *33*, 2807.

Table 10. Catalytic Ethene Conversion with the [η^5-(3-R)$C_5H_4CX_2$Ar]$TiCl_3$/MAO Catalyst Systems[a]



15 **3** **16** **17**

catalyst (R, X, Ar)	C_6 products, g (wt %)	C_{10} products, g (wt %)	PE, g (wt %)	productivity C_6 products[b]	trimerizn products, wt %	trimerizn productivity[c]
1 (H, Me, Ph)	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	110
10 (H, $[CH_2]_5$, Ph)	24.4 (87)	2.9 (10)	0.6 (2.0)	650	97	125
15 ($SiMe_3$, $[CH_2]_5$, Ph)	33.9 (84)	5.2 (13)	1.2 (3.0)	905	97	177
3 (H, Me, 3,5-$Me_2C_6H_3$)	7.9 (93)	0.1 (4)	0.1 (1.3)	210	97	38
16 ($SiMe_3$, Me, 3,5-$Me_2C_6H_3$)	40.1 (84)	7.0 (15)	0.3 (0.6)	1070	99	211
17 (CMe_3, Me, 3,5-$Me_2C_6H_3$)	24.4 (91)	1.6 (6)	0.7 (2.8)	650	97	121

[a] Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In g of C_6 product/((mmol of Ti) bar h). [c] In mol of olefinic bonds trimerized/((mmol of Ti) h).

ment of methyl subtituents on the aryl group was seen to lead to a decrease in C_6 productivity relative to **1**/MAO (for the catalyst with the 3,5-$Me_2C_6H_3$ group (**3**) a reduction by 62%). Remarkably, the catalyst [η^5-(3-$SiMe_3$)$C_5H_3CMe_2$-3,5-$Me_2C_6H_3$]$TiCl_3$ (**16**)/MAO, combining Cp substitution with aryl substitution, turned out to be the most active catalyst of all (Table 10), with an increase in the rate of C_6 production by 92% relative to **1**/MAO and a very high selectivity for the combined trimerization products (99%). Aryl substitution in the *tert*-butylcyclopentadienyl derivatives [η^5-(3-CMe_3)C_5H_3-CMe_2Ar]$TiCl_3$/MAO (Ar = Ph (**13**), 3,5-$Me_2C_6H_3$ (**17**)) has no effect on initial ethene uptake rate but significantly improves catalyst stability, as can be seen from the ethene uptake profile, affording a catalyst with comparable productivity to **1**/MAO over a 30 min run period. A judicious combination of substituents on the key positions (backbone, cyclopentadienyl, and arene) can thus improve the three major parameters in the catalytic trimerization process: activity, selectivity, and stability. The precise interplay of steric and electronic effects is as yet unclear and warrants further investigation.

Conclusions

We have identified a catalyst system, (η^5-$C_5H_4CMe_2R$)-$TiCl_3$/MAO, that by attachment of a pendant arene group to the cyclopentadienyl ancillary ligand (R = aryl) can be transformed from an ethene polymerization catalyst into a selective ethene trimerization catalyst. The intrinsic selectivity for ethene trimerization of the catalytic species is essentially independent of solvent and cocatalyst, and hemilabile behavior of the cyclopentadienyl−arene ancillary ligand appears to be essential for obtaining this high selectivity for trimerization.

We have shown that a wide range of titanium precatalysts of the type [η^5-C_5H_3R−(B)−Ar]$TiCl_3$ can be activated with MAO to effect catalytic ethene trimerization (summarized in Table 11). The nature of the bridging moiety (B) between the cyclopentadienyl and the arene group is crucial for obtaining a good selectivity in 1-hexene production. Thus far, only disubstituted C_1 bridges have afforded highly selective and active ethene

Table 11. Overview of Trimerization Activity and Selectivity with [η^5-(3-R)C_5H_3−(B)−Ar]$TiCl_3$/MAO Catalyst Systems[a]

precatalyst	R	B	Ar	trimerizn products, wt %	trimerizn productivity[b]
1	H	CMe_2	Ph	97	110
2	H	CMe_2	4-Me-C_6H_4	98	75
3	H	CMe_2	3,5-Me_2-C_6H_3	97	38
6	H	CH_2	Ph	<51	
7	H	$SiMe_2$	Ph	<43	
8	H	CMe_2CH_2	Ph	86	6
9	H	CEt_2	Ph	95	92
10	H	C[$(CH_2)_5$]	Ph	97	125
11	H	C=CH_2	Ph	95	87
12	$SiMe_3$	CMe_2	Ph	96	130
13	CMe_3	CMe_2	Ph	94	73
14	CMe_2Ph	CMe_2	Ph	96	59
15	$SiMe_3$	C[$(CH_2)_5$]	Ph	97	177
16	$SiMe_3$	CMe_2	3,5-Me_2-C_6H_3	99	211
17	CMe_3	CMe_2	3,5-Me_2-C_6H_3	97	121

[a] Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. [b] In mol of olefinic bonds trimerized/((mmol of Ti) h).

trimerization catalysts. Apparently, the conformational constraints imposed by the bridging unit are of major importance to catalyst performance. The introduction of additional substituents on the cyclopentadienyl moiety can influence both catalyst activity and stability. The introduction of a trimethylsilyl substituent is highly favorable for catalyst activity, whereas the addition of a second CMe_2Ph substituent greatly increases catalyst stability (albeit at the cost of a lower activity). Combining two ligand variations at a time shows in some cases a significant positive nonlinear additivity of the substituent effects on catalyst activity. In addition, steric effects can be employed to improve the selectivity for formation of a single monomethyl-branched α-olefin product in the cotrimerization of ethene with 1-alkenes.

Although some ethene oligomerization processes that produce 1-hexene in excess of the amount expected from Schulz−Flory product distributions and ethene polymerization catalysts that produce branched polyethenes are known (e.g., for certain Ziegler-type catalyst sys-

tems),[33] to our knowledge the present system is the first highly active ethene trimerization catalyst that is not based on chromium. Very recently catalyst systems for ethene trimerization based on $TaMe_2Cl_3$ and $(arene)_2$-VX (X = Br, Cl, BPh_4) were reported that show good selectivity for 1-hexene, but their activities are at least 2 orders of magnitude smaller than those of the titanium catalyst systems described here. The catalyst precursors, substituted mono(cyclopentadienyl)titanium trichloride complexes, are readily synthesized, and ligand variations can be easily introduced. They may provide a well-defined, highly active alternative to the currently available chromium-based ethene trimerization catalysts.

Experimental Section

Materials and Methods. All experiments were carried out under a purified nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (Aldrich, Acros) were either used as received ($CDCl_3$) or dried over Na/K alloy and vacuum-transferred before use (C_6D_6, THF-d_8). Cyclooctane (Aldrich, used as internal standard in the catalytic ethene conversion experiments) and *n*-octane (Aldrich) were distilled from sodium, and 1-octene (Aldrich) was distilled from CaH_2 prior to use. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å) under a nitrogen atmosphere prior to use. Diethyl ether and THF (Aldrich, anhydrous) were dried over Al_2O_3 (Fluka), and pentane, hexane, and methylene chloride (Aldrich, anhydrous) were dried over molecular sieves (Aldrich, 4 Å) under a nitrogen atmosphere before use. Ethene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å).

The compounds $C_5H_4(SiMe_3)CMe_2$-4-MeC_6H_4,[34] $[C_5H_4C(=CH_2)Ph]Li$,[14] 3-(α,α-dimethylbenzyl)-6,6-dimethylfulvene,[35] and $B(C_6F_5)_3$[36] were prepared according to published procedures. 6,6-Diethylfulvene was prepared from cyclopentadiene and 3-pentanone analogously to the procedure described for 6,6-pentamethylenefulvene,[37] and 3-*tert*-butyl-6,6-dimethylfulvene was prepared from *tert*-butylcyclopentadiene and acetone analogously to 3-(α,α-dimethylbenzyl)-6,6-dimethylfulvene.[35] The titanium complexes (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ (**1**),[9a] (η^5-C_5H_4-CMe_2-3,5-$Me_2C_6H_3$)$TiCl_3$ (**3**),[10] (η^5-$C_5H_4CMe_3$)$TiCl_3$ (**4**),[38] (η^5-$C_5H_4CMe_2Ph$)$TiMe_3$ (**5**),[9a] (η^5-$C_5H_4CH_2Ph$)$TiCl_3$ (**6**),[9c] (η^5-C_5H_4-$SiMe_2Ph$)$TiCl_3$ (**7**),[9a] and (η^5-$C_5H_4CMe_2CH_2Ph$)$TiCl_3$ (**8**)[9a] were prepared as reported previously. A toluene solution of MAO (9.8 wt % Al, Akzo Nobel Chemicals), MAO supported on silica (5 wt %, Witco), and $[PhNMe_2H][B(C_6F_5)_4]$ (Akzo Nobel Chemicals) were used as received.

NMR spectra were recorded on Varian Gemini 200/300 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ^1H NMR spectra were referenced to resonances of residual protons in the deuterated solvents (δ 7.15 ppm for C_6D_6, δ 7.24 ppm for $CDCl_3$). The ^{13}C NMR spectra were referenced to the carbon resonances of the deuterated solvent (δ 128 ppm for C_6D_6). Chemical shifts (δ) are given relative to tetramethylsilane (downfield shifts are positive); *J* values are given in hertz. GC analyses were performed on an HP 6890 instrument equipped with an HP-1 dimethylpolysiloxane column (19095 Z-123). GC/MS analyses were conducted using an HP 5973 mass-selective detector attached to an HP 6890 GC instrument. DSC analyses were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Given values are the average of at least two independent determinations.

Preparation of (η^5-$C_5H_4CMe_2$-4-MeC_6H_4)$TiCl_3$ (2). To a solution of 2.60 g (9.6 mmol) of $C_5H_4(SiMe_3)CMe_2$-4-MeC_6H_4 in 40 mL of methylene chloride at −30 °C was added dropwise 1.06 mL (1.8 g, 10 mmol) of titanium tetrachloride. The brown-red suspension was warmed to room temperature and was stirred overnight. The solvent was removed in vacuo, and the residue was stirred with 20 mL of pentane, which was subsequently pumped off. Extraction with methylene chloride and concentration and cooling of the extract to −40 °C afforded 2.32 g (6.6 mmol, 69%) of **2** as brown crystals. ^1H NMR (300 MHz, C_6D_6): δ 6.88 (d, $^3J_{HH}$ = 8.1, 2H, Ar *H*), 6.80 (d, $^3J_{HH}$ = 8.4, 2H, Ar *H*), 6.31 (ps t, $^3J_{HH}$ = 2.4, 2H, Cp *H*), 6.00 (ps t, $^3J_{HH}$ = 2.4, 2H, Cp *H*), 2.07 (s, 3H, ArCH_3), 1.56 (s, 6H, $C(CH_3)_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 154.6 (Ar C_{ipso}), 145.2 (Cp C_{ipso}), 136.1 (Ar *p*-C_{ipso}), 129.3, 126.1 (Ar *o*- and *m*-*C*H), 123.3, 121.7 (Cp *C*H), 40.6 ($C(CH_3)_2$), 28.8 ($C(CH_3)_2$), 20.7 (ArCH_3). Anal. Calcd for $C_{15}H_{17}TiCl_3$: C, 51.25; H, 4.87; Ti, 13.62. Found: C, 51.49; H, 4.89; Ti, 13.54.

Preparation of $C_5H_4(SiMe_3)CEt_2Ph$. To a solution of 4.85 g (58 mmol) of PhLi in 200 mL of diethyl ether, cooled to −50 °C, was added dropwise 8.0 g (60 mmol) of 6,6-diethylfulvene. The reaction mixture was warmed to room temperature and was stirred for 3 h. The yellow solution was then cooled with an ice bath, and 7.6 mL (6.5 g, 60 mmol) of trimethylsilyl chloride was added dropwise. The mixture was warmed to room temperature and was stirred overnight. The reaction mixture was poured into 250 mL of ice−water. The water layer was extracted with 2 × 100 mL of light petroleum, after which the combined organic layers were rinsed with 200 mL of brine. The organic phase was dried on $MgSO_4$. After the low-boiling volatiles were evaporated in vacuo, the residue was distilled using a Kugelrohr apparatus. The product was distilled at 110 °C at 0.5 Torr as a mixture of isomers. Yield: 9.21 g (32 mmol, 55%). ^1H NMR (300 MHz, $CDCl_3$, main isomer): δ 7.28 (m, 4H, Ph *o*- and *m*-*H*), 7.18 (m, 1H, Ph *p*-*H*), 6.40 (m, 1H, Cp *H*), 6.31 (s, 1H, Cp *H*), 6.22 (m, 1H, Cp *H*), 3.27 (s, 1H, Cp *H*), 2.02 (m, 4H, CH_2CH_3), 0.72 (m, 6H, CH_2CH_3), 0.06 (s, 9H, Si-$(CH_3)_3$).

Preparation of (η^5-$C_5H_4CEt_2Ph$)$TiCl_3$ (9). To a solution of 6.30 g (22 mmol) of $C_5H_4(SiMe_3)CEt_2Ph$ in 40 mL of methylene chloride, cooled to −40 °C, was added 2.45 mL (4.2 g, 22 mmol) of $TiCl_4$. The mixture was warmed to room temperature and was stirred overnight. The methylene chloride was removed in vacuo, and the residue was stirred with 50 mL of pentane, which was subsequently pumped off. Extracting with methylene chloride and cooling to −60 °C afforded red-brown crystals of the title compound. Yield: 5.63 g (15.3 mmol, 70%). ^1H NMR (300 MHz, C_6D_6): δ 7.24 (d, $^3J_{HH}$ = 7.3, 2H, Ph *o*-*H*), 7.17 (t, $^3J_{HH}$ = 7.3, 2H, Ph *m*-*H*), 7.06 (t, $^3J_{HH}$ = 7.3, 1H, Ph *p*-*H*), 6.26 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 6.04 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 2.06 (m, 2H, CH_2CH_3), 1.86 (m, 2H, CH_2CH_3), 0.51 (t, $^3J_{HH}$ = 7.3, 6H, CH_2CH_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 154.8, 142.1 (Ph and Cp C_{ipso}), 128.8 (Ph *o*-*C*H), 128.3 (Ph *m*-*C*H, overlap with solvent), 127.2 (Ph *p*-*C*H), 123.1, 121.8 (Cp *C*H), 48.6 ($C(CH_2CH_3)_2$), 29.3 ($C(CH_2CH_3)_2$), 8.5 ($C(CH_2CH_3)_2$). Anal. Calcd for $C_{16}H_{19}TiCl_3$: C, 52.57; H, 5.24; Ti, 13.10. Found: C, 52.75; H, 5.27; Ti, 12.99.

Preparation of $C_5H_4(SiMe_3)C[(CH_2)_5]Ph$. To a solution of 4.00 g (48 mmol) of PhLi in 200 mL of diethyl ether, cooled to −50 °C, was added dropwise 6.95 g (48 mmol) of 6,6-pentamethylenefulvene. The reaction mixture was warmed to room temperature and was stirred for 3 h. Subsequently the yellow solution was cooled with an ice bath and 6.4 mL (5.5 g,

(33) For example, see: Murtuza, S.; Harkins, S. B.; Long, G. S.; Sen, A. *J. Am. Chem. Soc.* **2000**, *122*, 1867 and references therein.
(34) Sassmannshausen, J. *Organometallics* **2000**, *19*, 482.
(35) Gutmann, S.; Burger, P.; Hund, H. U.; Hofmann, J.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 343.
(36) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218.
(37) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.
(38) Hart, S. L.; Duncalf, D. J.; Hastings, J. J.; McCamley, A.; Taylor, P. C. *J. Chem. Soc. Dalton Trans.* **1996**, 2843.

51 mmol) of trimethylsilyl chloride was added dropwise. The mixture was warmed to room temperature and was stirred overnight. The reaction mixture was poured into 250 mL of ice−water. The water layer was extracted with 2 × 100 mL of light petroleum, after which the combined organic layers were rinsed with 200 mL of brine. The organic phase was dried on $MgSO_4$. After the low-boiling volatiles were evaporated in vacuo, the residue was distilled using a Kugelrohr apparatus. The product was distilled at 165 °C at 0.4 Torr as a mixture of isomers. Yield: 8.96 g (30 mmol, 63%). ^{1}H NMR (300 MHz, $CDCl_3$, main isomer): δ 7.40 (m, 2H, Ph *o-H*), 7.33 (m, 2H, Ph *m-H*), 7.15 (m, 1H, Ph *p-H*), 6.43 (m, 2H, Cp *H*), 6.15 (s, 1H, Cp *H*), 3.27 (s, 1H, Cp *H*), 2.17 (m, 4H, α-CH_2), 1.65−1.40 (m, 6H, β- and γ-CH_2), −0.03 (s, 9H, Si(CH_3)$_3$).

Preparation of {η^5-$C_5H_4C[(CH_2)_5]Ph$}$TiCl_3$ (10). Titanium tetrachloride (1.4 mL, 2.4 g, 12.7 mmol) was added to a solution of 3.70 g (12.5 mmol) of $C_5H_4(SiMe_3)C[(CH_2)_5]Ph$ in 40 mL of methylene chloride, cooled to −40 °C. The reaction mixture was warmed to room temperature and was stirred overnight. The methylene chloride was removed in vacuo, and the residue was stirred with 30 mL of pentane, which was subsequently pumped off. The residue was extracted with methylene chloride. Crystallization from a 1:1 (v/v) mixture of CH_2Cl_2 and pentane afforded red-brown crystals of the title compound in 78% yield (3.68 g, 9.7 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ 7.16−7.06 (m, 4H, Ph *o-* and *m-H*), 7.01 (m, 1H, Ph *p-H*), 6.31 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 5.97 (ps t, $^3J_{HH}$ = 2.8, 2H, Cp *H*), 2.45 (d, $^2J_{HH}$ = 13.2, 2H, α-CH_{eq}), 1.88 (m, 2H, α-CH_{ax}), 1.37 (br, 3H, β- and γ-CH_2), 1.25−1.05 (m, 3H, β- and γ-CH_2). ^{13}C NMR (75.4 MHz, C_6D_6): δ 156.0, 142.1 (Ph and Cp C_{ipso}), 129.2 (Ph *o-C*H), 127.9 (Ph *m-C*H), 126.8 (Ph *p-C*H), 123.2, 120.9 (Cp *C*H), 45.1 (*C*[$(CH_2)_5$]), 35.8 (α-CH_2), 26.1 (γ-CH_2), 22.4 (β-CH_2). Anal. Calcd for $C_{17}H_{19}TiCl_3$: C, 54.08; H, 5.07; Ti, 12.69. Found: C, 53.93; H, 4.90; Ti, 12.62.

Preparation of [η^5-$C_5H_4C(=CH_2)Ph$]$TiCl_3$ (11). To a solution of 0.61 mL (1.06 g, 5.6 mmol) of titanium tetrachloride in 40 mL of methylene chloride, cooled to −50 °C, was added 1.80 g (5.6 mmol) of [$C_5H_4C(=CH_2)Ph$]Li. The reaction mixture was warmed to room temperature and was stirred overnight. The volatiles were removed in vacuo, and the green-black residue was stirred with 30 mL of pentane, which was subsequently pumped off. Extraction with pentane afforded small amounts of the analytically pure title compound as dark red crystals. Isolated yield: 0.25 g (0.8 mmol, 14%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.2−7.05 (m, 5H, Ph *H*), 6.35 (ps t, $^3J_{HH}$ = 2.7, 2H, Cp *H*), 6.01 (ps t, $^3J_{HH}$ = 2.7, 2H, Cp *H*), 5.58 (s, 1H, =CH_2), 5.20 (s, 1H, =CH_2). ^{13}C NMR (75.4 MHz, C_6D_6): δ 142.5, 139.7, 139.6 (Ph, Cp C_{ipso} and *C*=CH_2), 128.8, 128.7, 128.5 (Ph *C*H), 123.4, 121.1, 120.5 (Cp *C*H and =CH_2). Anal. Calcd for $C_{13}H_{11}TiCl_3$: C, 48.57; H, 3.45; Ti, 14.90. Found: C, 48.71; H, 3.55; Ti, 14.78.

Preparation of $C_5H_3(SiMe_3)_2CMe_2Ph$. To a solution of 2.25 g (11.8 mmol) of [$C_5H_4CMe_2Ph$]Li in 50 mL of diethyl ether and 20 mL of THF, cooled in ice−water, was added dropwise 1.5 mL (1.3 g, 11.9 mmol) of Me_3SiCl. The mixture was warmed to room temperature and was stirred overnight. The yellow solution was cooled in ice−water, and 4.8 mL (12 mmol) of a 2.5 M *n*-BuLi solution in hexanes was added. After it was warmed to room temperature, the mixture was stirred for 4 h. The white suspension was cooled in ice−water, and 1.6 mL (1.4 g, 12.7 mmol) of Me_3SiCl was added dropwise. The mixture was warmed to room temperature and stirred overnight. The yellow suspension was poured into 125 mL of ice−water. The water layer was extracted with 50 mL of light petroleum, and the combined organic layers were dried on $MgSO_4$. After evaporation of low-boiling volatiles, the residue was distilled using a Kugelrohr apparatus. The product was distilled at 115 °C at 0.8 Torr. Yield: 2.87 g (8.7 mmol, 74%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4−7.1 (m, 5H, Ph *H*), 6.40 (d, $^3J_{HH}$ = 2.2, 2H, Cp *H*), 6.20 (t, $^3J_{HH}$ = 2.1, 1H, Cp *H*), 1.53 (s, 6H, C(CH_3)$_2$), −0.03 (s, 18H, Si(CH_3)$_3$).

Preparation of [η^5-(3-$SiMe_3$)$C_5H_3CMe_2Ph$]$TiCl_3$ (12). To a solution of 0.92 mL (1.6 g, 8.4 mmol) of $TiCl_4$ in 50 mL of methylene chloride, cooled to −50 °C, was added 2.75 g (8.4 mmol) of $C_5H_3(SiMe_3)_2CMe_2Ph$. The reaction mixture was warmed to room temperature and was stirred overnight. The volatiles were removed in vacuo, and the residue was stirred with 15 mL of pentane, which was subsequently pumped off. Extracting with methylene chloride and cooling to −60 °C afforded 2.76 g (6.7 mmol, 80%) of the title compound. ^{1}H NMR (300 MHz, C_6D_6): δ 7.1−6.85 (m, 5H + 1H, Ph *H* and Cp *H*), 6.57 (m, 1H, Cp *H*), 6.53 (m, 1H, Cp *H*), 1.63 (s, 6H, C(CH_3)$_2$), 0.12 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 158.5, 148.5, 144.1 (Ph and Cp C_{ipso}), 128.7, 128.6, 126.7, 126.1, 124.6 (Ph *C*H and Cp *C*H), 41.2 (*C*(CH_3)$_2$), 29.3, 29.0 (C(CH_3)$_2$), −0.8 (Si(CH_3)$_3$). Anal. Calcd for $C_{17}H_{23}SiTiCl_3$: C, 49.84; H, 5.66; Ti, 11.69. Found: C, 49.70; H, 5.68; Ti, 11.59.

Preparation of [$C_5H_3(CMe_3)CMe_2Ph$]Li. To a solution of 3.80 g (45 mmol) of phenyllithium in 60 mL of diethyl ether, cooled to −40 °C, was added 7.4 g (46 mmol) of 3-*tert*-butyl-6,6-dimethylfulvene. The reaction mixture was warmed to room temperature and was stirred overnight. The volatiles were removed in vacuo. The yellow oil was suspended in 40 mL of *n*-hexane and was refluxed for 4 h. The resulting off-white solid was filtered off and repeatedly rinsed with pentane to afford 5.50 g (22 mmol, 49%) of product. ^{1}H NMR (300 MHz, C_6D_6/THF-d_8): δ 7.53 (d, $^3J_{HH}$ = 7.0, 2H, Ph *o-H*), 7.13 (t, $^3J_{HH}$ = 7.3, 2H, Ph *m-H*), 6.98 (m, 1H, Ph *p-H*), 5.85 (m, 2H, Cp *H*), 5.79 (m, 1H, Cp *H*), 1.81 (s, 6H, C(CH_3)$_2$), 1.45 (s, 9H, C(CH_3)$_3$).

Preparation of [η^5-(3-CMe_3)$C_5H_3CMe_2Ph$]$TiCl_3$ (13). To a solution of 1.47 g (6.0 mmol) of [$C_5H_4(CMe_3)CMe_2Ph$]Li in 30 mL of methylene chloride, cooled to −20 °C, was added dropwise 0.70 mL (1.2 g, 6.3 mmol) of $TiCl_4$. The red-brown solution was warmed to room temperature and was stirred overnight. The solvent was removed in vacuo, and the residue was stirred with 20 mL of pentane, which was subsequently pumped off. Extraction with toluene afforded a brown oil that could not be crystallized from pentane, hexane, toluene, or methylene chloride. The oil was repeatedly rinsed with cold pentane to give 1.98 g (5.0 mmol, 83%) of product (about 95% purity as indicated by NMR spectroscopy). ^{1}H NMR (300 MHz, C_6D_6): δ 7.1−7.0 (m, 3H, Ph *m-* and *p-H*), 6.87 (d, $^3J_{HH}$ = 7.0, 2H, Ph *o-H*), 6.60 (ps t, $^3J_{HH}$ = 2.4, 1H, Cp *H*), 6.40 (ps t, $^3J_{HH}$ = 3.3, 1H, Cp *H*), 6.29 (ps t, $^3J_{HH}$ = 2.9, 1H, Cp *H*), 1.64 (s, 3H, C(CH_3)$_2$), 1.63 (s, 3H, C(CH_3)$_2$), 1.04 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 157.5, 156.1, 148.8 (Ph and Cp C_{ipso}), 128.6, 126.6, 126.1 (Ph *C*H), 120.5, 120.0, 119.6 (Cp *C*H), 41.6 (*C*(CH_3)$_2$), 34.7 (*C*(CH_3)$_3$), 30.4 (C(CH_3)$_3$), 28.9, 28.7 (C(CH_3)$_2$).

Preparation of [C_5H_3-1,3-$(CMe_2Ph)_2$]Li. To a suspension of 2.28 g (27.1 mmol) of PhLi in 50 mL of *n*-hexane was added 6.14 g (27.4 mmol) of 3-(α,α-dimethylbenzyl)-6,6-dimethylfulvene. The mixture was refluxed for 5 h. The precipitate was poured onto a glass frit and rinsed with 2 × 20 mL of pentane. Drying in vacuo yielded 4.18 g (13.6 mmol, 50%) of an off-white solid. ^{1}H NMR (300 MHz, C_6D_6/THF-d_8): δ 7.55 (d, $^3J_{HH}$ = 8.2, 4H, Ph *o-H*), 7.16 (m, 4H, Ph *m-H*), 7.01 (m, 2H, Ph *p-H*), 5.87 (m, 1H, Cp *H*), 5.83 (m, 2H, Cp *H*), 1.79 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (75.4 MHz, C_6D_6/THF-d_8): δ 154.9, 129.0 (Ph and Cp C_{ipso}), 127.8, 126.7, 124.7 (Ph *C*H), 100.8, 99.8 (Cp *C*H), 39.8 (*C*(CH_3)$_2$), 32.5 (C(CH_3)$_2$).

Preparation of [η^5-C_5H_3-1,3-$(CMe_2Ph)_2$]$TiCl_3$ (14). To a solution of 1.31 g (4.2 mmol) of [C_5H_3-1,3-$(CMe_2Ph)_2$]Li in 30 mL of methylene chloride, cooled to −40 °C, was added dropwise 0.47 mL (0.8 g, 4.2 mmol) of $TiCl_4$. The dark brown solution was warmed to room temperature and was stirred overnight. The solvent was removed in vacuo, and the residue was stirred with 40 mL of pentane, which was subsequently pumped off. The residue was extracted with 50 mL of toluene, which was replaced by a 1:1 (v/v) mixture of methylene chloride and pentane (30 mL in total). Cooling to −40 °C afforded 0.22 g (0.5 mmol, 12%) of the title compound. ^{1}H NMR (300 MHz, C_6D_6): δ 6.98 (m, 2H, Ph *p-H*), 6.96 (m, 4H, Ph *m-* or *o-H*),

6.70 (m, 4H, Ph *m*- or *o*-*H*), 6.50 (m, 1H, Cp *H*), 6.40 (d, $^3J_{HH}$ = 2.6, 2H, Cp *H*), 1.60 (s, 6H, C(CH_3)$_2$), 1.54 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 156.2, 148.8 (Ph and Cp C_{ipso}), 128.4, 126.5, 126.0 (Ph *C*H), 121.5, 120.5 (Cp *C*H), 41.7 (*C*(CH$_3$)$_2$), 28.5, 28.4 (C(*C*H$_3$)$_2$). Anal. Calcd for $C_{23}H_{25}TiCl_3$: C, 60.62; H, 5.53. Found: C, 60.16; H, 5.56.

Preparation of $C_5H_3(SiMe_3)_2C[(CH_2)_5]Ph$. To a solution of 1.67 g (7.3 mmol) of {$C_5H_4C[(CH_2)_5]Ph$}Li in 70 mL of diethyl ether, cooled with ice−water, was added dropwise 0.8 mL (0.7 g, 6.4 mmol) of trimethylsilyl chloride. The reaction mixture was warmed to room temperature and was stirred overnight. The white suspension was cooled to −30 °C, and 7.3 mmol of a 2.5 M solution of *n*-BuLi in hexanes was added dropwise. After the mixture was stirred for 3 h at ambient temperature, the reaction vessel was placed in ice−water and 0.9 mL (0.8 g, 7.4 mmol) of trimethylsilyl chloride was added. The reaction mixture was warmed to room temperature and was stirred overnight. The mixture was poured into 100 mL of ice−water. The water layer was extracted twice with 50 mL portions of light petroleum, and the combined organic layers were dried over $MgSO_4$. Kugelrohr distillation at 160 °C and 0.4 Torr yielded 1.28 g (3.5 mmol, 55%) of the title compound. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45−7.1 (m, 5H, Ph *H*), 6.50 (m, 1H, Cp *H*), 6.39 (m, 1H, Cp *H*), 6.18 (m, 1H, Cp *H*), 2.2 (m, 4H, α-CH_2), 1.55 (m, 6H, *β*- and *γ*-CH_2), −0.07 (s, 18H, Si(CH_3)$_3$).

Preparation of {η^5-(3-SiMe$_3$)$C_5H_3C[(CH_2)_5]Ph$}$TiCl_3$ (15). To a solution of 0.34 mL (0.6 g, 3.2 mmol) of titanium tetrachloride in 40 mL of methylene chloride, cooled to −40 °C, was added dropwise 1.20 g (3.3 mmol) of C_5H_3-(SiMe$_3$)$_2$C[(CH$_2$)$_5$]Ph. The reaction mixture was warmed to room temperature and was stirred overnight. The volatiles were removed in vacuo, and the residue was stripped with pentane. Extraction with methylene chloride yielded red-brown crystals. Yield: 0.68 g (1.5 mmol, 47%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.13 (m, 4H, Ph *o*- and *m*-*H*), 7.01 (m, 1H, Cp *H*), 6.93 (m, 1H, Ph *p*-*H*), 6.45 (m, 2H, Cp *H*), 2.54 (m, 2H, α-CH_{eq}), 2.07, 1.86 (m, 1H each, α-CH_{ax}), 1.4 (br, 3H, *β*- and *γ*-CH_2), 1.15 (br, 3H, *β*- and *γ*-CH_2), 0.13 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 160.3, 143.6, 142.2 (Ph and Cp C_{ipso}), 129.1, 128.7, 126.8, 126.7, 123.7 (Ph *C*H and Cp *C*H), 45.4 (*C*[(CH$_2$)$_5$]), 36.6, 35.7 (α-*C*H$_2$), 26.1 (*γ*-*C*H$_2$), 22.4 (*β*-*C*H$_2$), −0.8 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{20}H_{27}SiTiCl_3$: C, 53.41; H, 6.05; Ti, 10.65. Found: C, 52.83; H, 6.08; Ti, 10.52.

Preparation of $C_5H_3(SiMe_3)_2CMe_2$-3,5-$Me_2C_6H_3$. To a solution of 1.15 g (5.3 mmol) of [$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$]Li in 50 mL of diethyl ether, cooled with ice−water, was added dropwise 0.7 mL (0.6 g, 5.5 mmol) of trimethylsilyl chloride. The reaction mixture was warmed to room temperature and was stirred overnight. The white suspension was cooled to −30 °C, and 5.4 mmol of a 2.5 M solution of *n*-BuLi in hexanes was added dropwise. After the mixture was stirred for 3 h at ambient temperature, the reaction vessel was placed in ice−water and 0.8 mL (0.7 g, 6.4 mmol) of trimethylsilyl chloride was added. The reaction mixture was warmed to room temperature and was stirred overnight. The mixture was poured into 100 mL of ice−water. The water layer was extracted twice with 50 mL portions of light petroleum, and the combined organic layers were dried over $MgSO_4$. Kugelrohr distillation at 160 °C and 0.4 Torr yielded 1.26 g (3.5 mmol, 66%) of the title compound. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.90 (s, 2H, Ar *o*-*H*), 6.78 (s, 1H, Ar *p*-*H*), 6.37 (m, 2H, Cp *H*), 6.19 (m, 1H, Cp *H*), 2.24 (s, 6H, ArCH_3), 1.51 (s, 6H, C(CH_3)$_2$), −0.05 (s, 18H, Si(CH_3)$_3$).

Preparation of [η^5-(3-SiMe$_3$)$C_5H_3CMe_2$-3,5-$Me_2C_6H_3$]-$TiCl_3$ (16). To a solution of 0.35 mL (0.6 g, 3.2 mmol) of titanium tetrachloride in 40 mL of methylene chloride, cooled to −40 °C, was added dropwise 1.18 g (3.3 mmol) of C_5H_3(SiMe$_3$)$_2$CMe$_2$-3,5-$Me_2C_6H_3$. The reaction mixture was warmed to room temperature and was stirred overnight. The volatiles were removed in vacuo, and the residue was stripped with pentane. Extraction with pentane yielded 1.02 g (2.3 mmol, 72%) of light brown crystals. ^{1}H NMR (300 MHz, C_6D_6): δ 6.96 (m, 1H, Cp *H*), 6.69 (s, 2H, Ar *o*-*H*), 6.64 (m, 2H, Cp *H* and Ar *p*-*H*), 6.55 (m, 1H, Cp *H*), 2.08 (s, 6H, ArCH_3), 1.70 (s, 6H, C(CH_3)$_2$), 0.13 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 159.1, 148.5, 144.1 (Ar and Cp C_{ipso}), 137.9 (Ar *m*-C_{ipso}), 128.8, 128.4, 127.8, 124.7, 124.1 (Ar *C*H and Cp *C*H), 41.2 (*C*(CH$_3$)$_2$), 29.3, 29.2 (C(*C*H$_3$)$_2$), 21.5 (Ar*C*H$_3$), −0.9 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{19}H_{27}SiTiCl_3$: C, 52.13; H, 6.22; Ti, 10.94. Found: C, 51.72; H, 6.24; Ti, 10.76.

Preparation of [C_5H_4(CMe$_3$)CMe_2-3,5-$Me_2C_6H_3$]Li. A solution of 1.88 g (17 mmol) of (3,5-dimethylphenyl)lithium in 40 mL of diethyl ether was cooled to −40 °C. An equimolar amount of 3-*tert*-butyl-6,6-dimethylfulvene (2.7 g) was added. The reaction mixture was warmed to room temperature and was stirred overnight. Removing the solvent in vacuo gave a yellow oil which solidified in refluxing hexane. The solid was repeatedly rinsed with pentane to yield 2.35 g (8.6 mmol, 51%) of the title compound. ^{1}H NMR (300 MHz, C_6D_6/THF-d_8): δ 7.17 (s, 2H, Ar *o*-*H*), 6.63 (s, 1H, Ar *p*-*H*), 5.81, 5.77, 5.71 (m, 1H each, Cp *H*), 2.13 (s, 6H, ArCH_3), 1.77 (s, 6H, C(CH_3)$_2$), 1.40 (s, 9H, C(CH_3)$_3$).

Preparation of [η^5-(3-CMe$_3$)$C_5H_3CMe_2$-3,5-$Me_2C_6H_3$]-$TiCl_3$ (17). To a solution of 1.54 g (5.6 mmol) of [C_5H_4(CMe$_3$)-CMe$_2$-3,5-$Me_2C_6H_3$]Li in 30 mL of methylene chloride, cooled to −20 °C, was added dropwise 0.65 mL (1.1 g, 5.8 mmol) of titanium tetrachloride. The mixture was warmed to room temperature and was stirred overnight. Removing the volatiles, stripping with pentane, and extracting with toluene afforded a brown oil. Repeated rinsing with cold pentane afforded 2.06 g (4.9 mmol, 88%) of the oil, which was 95% pure, as seen by NMR spectroscopy. ^{1}H NMR (300 MHz, C_6D_6): δ 6.7−6.5 (m, 2H, Ar *p*-*H* and Cp *H*), 6.63 (s, 2H, Ar *o*-*H*), 6.43 (t, $^3J_{HH}$ = 2.9, 1H, Cp *H*), 6.29 (t, $^3J_{HH}$ = 2.9, 1H, Cp *H*), 2.09 (s, 6H, ArCH_3), 1.70 (s, 3H, C(CH_3)$_2$), 1.69 (s, 3H, C(CH_3)$_2$), 1.05 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 157.3, 156.5, 149.0 (Ar and Cp C_{ipso}), 137.8 (Ar *m*-C_{ipso}), 124.6 (Ar *p*-*C*H), 124.1 (Ar *o*-*C*H), 120.6, 120.1, 119.5 (Cp *C*H), 41.7 (*C*(CH$_3$)$_2$), 34.7 (*C*(CH$_3$)$_3$), 30.4 (C(*C*H$_3$)$_3$), 29.0, 28.9 (C(*C*H$_3$)$_2$), 21.5 (Ar*C*H$_3$).

General Procedure for the Catalytic Ethene Conversions with MAO as Cocatalyst. A stainless steel 1 L autoclave (Medimex), fully temperature- and pressure-controlled and equipped with solvent and catalyst injection systems, was preheated in vacuo for 45 min at 100 °C prior to use. The reactor was cooled to the desired temperature, charged with 200 mL of toluene, and pressurized with ethene. After equilibration for 15 min, the appropriate amount of MAO/toluene was injected, together with 25 mL of toluene. Subsequently, a mixture of 2.50 g of cyclooctane (internal standard) and 1.0 mL of a 15 mM stock solution of the titanium halide complex in toluene was injected, together with 25 mL of toluene, to start the reaction. During the reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. The run was ended by adding an aliquot of ethanol, and the reactor was vented. The remaining residual MAO was destroyed by adding further ethanol, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The polymer was stirred for 1 h in acidified ethanol, repeatedly rinsed with ethanol on a glass frit, and dried in vacuo at 70 °C overnight. For entry 2 in Table 1, the volatiles of the liquid fraction of the reaction mixture were removed on a rotary evaporator operating at 80 °C and 180 Torr to give 3.8 g of a fraction, predominantly containing the C_{10} isomers (^{1}H NMR spectroscopy showed that the sample contained about 10 mol % toluene and 10 mol % cyclooctane).

Procedure for the Catalytic Ethene Conversions using (η^5-$C_5H_4CMe_2Ph$)$TiMe_3$ (5) with $B(C_6F_5)_3$ or [$PhNMe_2H$][$B(C_6F_5)_4$] as Cocatalyst. A stainless steel 500 mL autoclave (Medimex), fully temperature- and pressure-controlled and equipped with solvent and catalyst injection

systems, was preheated in vacuo for 45 min at 100 °C. The reactor was cooled to the desired temperature, charged with 150 mL of toluene, and pressurized with ethene. After equilibration for 15 min, the appropriate amount of boron-based cocatalyst in 5 mL of toluene was injected, together with 25 mL of toluene. Subsequently, a mixture of 2.50 g of cyclooctane (internal standard) and 1.0 mL of a 15 mM stock solution of the titanium trimethyl complex in toluene was injected, together with 25 mL of toluene, to start the reaction. During the reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing the flow. The run was ended by venting the reactor, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The polymer was repeatedly rinsed with ethanol on a glass frit and was dried in vacuo at 70 °C overnight.

Procedure for the Catalytic Ethene Conversions using (η^5-$C_5H_4CMe_2Ph$)$TiMe_3$ (5) with MAO/SiO_2 as Cocatalyst. A stainless steel 1 L autoclave (Medimex), fully temperature- and pressure-controlled and equipped with solvent and catalyst injection systems, was preheated in vacuo for 45 min at 100 °C. The reactor was cooled to the desired temperature, charged with 200 mL of toluene, and pressurized with ethene. After equilibration for 15 min, a slurry of 2.05 g of silica with 5 wt % MAO in 10 mL of toluene was injected together with 30 mL of toluene. Subsequently, a mixture of 2.50 g of cyclooctane (internal standard) and 1.0 mL of a 15 mM stock solution of the titanium trimethyl complex in toluene was injected, together with 25 mL of toluene, to start the reaction. During reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. The run was ended by adding an aliquot of ethanol, and the reactor was vented. Remaining residual MAO was destroyed by adding further ethanol, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The amount of polymer, precipitated on the silica support, could not be quantified, since the suspended fine polymer/support particles could not be separated quantitatively from the liquid fraction.

Acknowledgment. We thank Mr. G. Alberda for the DSC analyses and Mr. A. Jekel for GC/MS and GPC analyses.

OM020765A